2.7 Isotope Analysis & Isotope Separation

Isotope ratios for specific elements can change locally due to geological, climatological, biological, chemical and physical processes during the history of the earth.

The analysis of isotope ratios is a unique tool for provenance studies as seen in previous examples.

Typical isotope ratios used for provenance studies:

\[
\begin{align*}
\frac{^{13}C}{^{12}C} & \quad \delta^{18}O = \left( \frac{O^{18}}{O^{16}} \right)_{\text{sample}} - 1 \cdot 1000 \%
\end{align*}
\]

Example: isotope distribution in different Greek quarries.
Determination of the Pb isotope ratio

Neutron activation technique on $^{204}$Pb or $^{208}$Pb?

$^{204}$Pb$(n,\gamma)^{205}$Pb;  $^{208}$Pb$(n,\gamma)^{209}$Pb;

Not possible since $^{205}$Pb and $^{209}$Pb have no characteristic $\gamma$ decay radiation!

Alternative method: isotope analysis by mass separation techniques!
Separation in magnetic fields

\[
\frac{m}{q} = \frac{B \cdot R}{\nu}; \quad m = \left(\frac{q \cdot B}{\nu}\right) \cdot R
\]

particles with velocity \(\nu\) are separated by \(m/q\) for a fixed magnetic field \(B\) and a spectrometer radius \(R\)
Example: Separation of $^{204}\text{Pb}$ and $^{208}\text{Pb}$

\[ \frac{m}{q} = m \frac{B \cdot R}{v} ; \quad m = \left( \frac{q \cdot B}{v} \right) \cdot R \]

\[ \frac{m_1}{m_2} = \left( \frac{q \cdot B}{v} \right) \cdot \frac{R_1}{R_2} = \frac{R_1}{R_2} \]

\[ \frac{204}{208} = \frac{R_1}{R_2} \quad \text{for} \quad R_2 = 1 \text{ m}; \]

\[ R_1 = \frac{204}{208} m = 0.98 \text{ m} \]

Separated $^{204}\text{Pb}$, $^{208}\text{Pb}$ beams
Mass Spectrum
Isotope Analyzer

Small sample of material with mass $<\mu g$ is ionized by sputter technique, accelerated and mass separated by sequence of magnetic and electrical fields
The Hittite empire had an extensive metallurgy and mining industry in the early bronze age, 1500-1300 BC.
Hittite Mining Site determination by lead (Pb) isotope analysis

Control over the mining sites was important for Hittite empire trade.

Origin of metal in artifact is determined by their $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratio.

Metal contain tin, copper, nickel and lead!
The importance of lead isotopes

There are 4 stable lead isotopes: $^{204}\text{Pb}$, $^{206}\text{Pb}$, $^{207}\text{Pb}$, $^{208}\text{Pb}$

Lead isotope distribution is not necessarily constant but may change if significant Uranium and Plutonium abundance exist in the ore material. Natural decay of these $\alpha$ unstable isotopes feed the Pb isotopes.
Natural decay chains & the feeding of Pb isotopes

- $^{206}\text{Pb}$
- $^{207}\text{Pb}$
- $^{208}\text{Pb}$
Pb isotopic ratio

Depending on chemical history and water content of ore material significant differences exist in abundances of long-lived “mother” U, Np, Pt elements in the ore material. This eventually leads to build-up of significant differences in lead “daughter” isotopic abundances, which often is characteristic for the mine site.

Present day lead = primeval lead + radiogenic lead

Simple evolution model:

\[ \frac{^{206}Pb}{^{204}Pb}(t) = \frac{^{206}Pb}{^{204}Pb}(t_p) + \mu \cdot (e^{\lambda_{238} \cdot t_p} - e^{-\lambda_{238} \cdot t}) \]

\[ \frac{^{207}Pb}{^{204}Pb}(t) = \frac{^{207}Pb}{^{204}Pb}(t_p) + \frac{\mu}{137.8} \cdot (e^{\lambda_{235} \cdot t_p} - e^{-\lambda_{235} \cdot t}) \]

\[ \frac{^{208}Pb}{^{204}Pb}(t) = \frac{^{208}Pb}{^{204}Pb}(t_p) + W \cdot (e^{\lambda_{232} \cdot t_p} - e^{-\lambda_{232} \cdot t}) \]

\( t_p \): time between origin of earth and last geological active period

\( \lambda_{238} \): decay constant of \(^{238}\text{U}\)

\( \lambda_{235} \): decay constant of \(^{235}\text{U}\)

\( \lambda_{232} \): decay constant of \(^{232}\text{Th}\)
Evolution model applied for US mines

Certain lead isotope ratios characterize original mines, the analysis of the lead isotope ratio reveals ancient trading routes.

Present isotope ratio parameters:

$$\mu = \frac{^{238}U}{^{204}Pb}$$

$$W = \frac{^{232}Th}{^{204}Pb}$$
Ancient ship trade ca 1500 BC
Difficulty of Underwater Archaeology
Egyptian trading vessel at Uluburun Kas
The Uluburun Wreck
Copper and tin ingots

Tin ingot

Copper ingots
Origin and destination?
Did the ship sail west or east

Origin of copper and tin can be tested on the mine specific lead isotope ratio in the ingots.

Typical lead ratio of Taurus mines

Typical lead ratio of ship ingots

Lead concentration in copper and tin
Trading Route
Food and Diet analysis

Important aspect in archaeology is migration and trade; isotope analysis of human remains such as bone and teeth delivers important information on diet and origin.

Isotope distribution in teeth and bone reflects characteristic isotope ratios (C, N, O, Sr) in food and water from local habitat. Teeth mineralize at early age, maintaining the isotopic signature from early age in teeth enamel. Bones adopt every twenty years. Comparison of teeth and bone isotope ratios indicates changes if a person has drastically changed its habitat.

\[ ^{18}O/^{16}O \] ratio decreases with altitude and with distance to coast due to mass difference in isotopes - fractionation
Depth analysis in teeth

Drilling and sequential isotope ratio analysis reveals fine structure, possibly due to migration habits.

tooth enamel is formed in early childhood ⇒ origin dentin & bone changes with time ⇒ death
Fractionation

Natural chemical or physical processes can fractionate the carbon isotopes during the up-take and alter the $^{13}\text{C} / ^{12}\text{C}$ and $^{14}\text{C} / ^{12}\text{C}$ isotopic ratios. This requires correction.

e.g. photosynthesis enriches lighter isotopes $\rightarrow$ carbon in plant has relatively higher $^{12}\text{C} / ^{14}\text{C}$ ratio than atmosphere.

Fractionation is expressed in terms of $\delta^{13}\text{C}$ which is a measure (in parts of a thousand ppm) of the deviation of the isotopic ratio $^{13}\text{C} / ^{12}\text{C}$ from a standard material (PDB belemnitella americana). Typical $\delta^{13}\text{C}$ vary between $+2$ppm to $-27$ppm and need to be determined for the material to be dated. Additional fractionation may occur during the chemical preparation of the sample.
Fractionation effects

fractionation term $\delta^{13}C$ is defined from $^{13}C/^{12}C$ isotopic ratios for the sample (sm) and the standard (st) as:

$$\delta^{13}C \equiv 1000 \cdot \left[ \frac{\left( \frac{^{13}C}{^{12}C} \right)_{sm}}{\left( \frac{^{13}C}{^{12}C} \right)_{st}} - 1 \right]$$

A negative value $\delta^{13}C$ means that the sample is isotopically lighter than the standard probe. A positive value means that the sample is enriched in the heavier isotope components.

For these corrections is assumed that the $^{14}C/^{13}C$ ratio scales with the $^{13}C/^{12}C$ ratio!
Excursion: fractionation and eating habits and its impact on dating bones

There are two different processes of photochemical assimilation of CO$_2$ in plants (photosynthesis cycles). This leads to quite different carbon fractionation values $\delta^{13}$C ranging from $\delta^{13}$C = -26.5‰ to $\delta^{13}$C = -12.5 ‰.

$C_3$ plants dominate the northern cooler regions of Europe and North America. The habitat of $C_4$ plants are the warmer regions in South- and Central America, Africa, and Australia.
Fractionation in food chain processes

bicarbonate in ocean water and in ground

CO$_2$ in air

plants

$\delta^{13}$C in bone collage

pure C$_4$ eaters

pure C$_3$ eaters

enrichment in $\delta^{13}$C in bone collage
North American Values

North American plants are predominantly C3 plants ⇒ fractionation values of $\delta^{13}C = -21.4$ are observed in bone collages of plant and meat eating animals.

If additional C$_4$ plants - like corn – are consumed than will the $\delta^{13}C$ value increase accordingly. e.g. $\approx$10% corn ⇒ $\delta^{13}C \approx -20 \text{‰}$. Pure maize diet will result in $\delta^{13}C \approx -10 \text{‰}$.

Is sea food consumed drastic changes occur since the ocean food chain is characterized by different fractionation processes leading to $\delta^{13}C \approx -18 \text{‰}$. 


Ancient eating habits

The fractionation analysis of bone material with parallel $^{14}$C dating can help to identify changing eating habits.

Example: increase of corn consumption ($C_4$ plant) by population due to the corn migration into North America. The values result from bone analysis of human skeletons. At 1500 AD: ~75% corn consumption.
Sea food chains

bicarbonate in ocean water and in ground

PDB-Standard

CO₂ in air

plankton similar C₃ (-17.8)

mammals fish, crabs, and coastal fauna

bone material of coastal residents ocean proteins

nutrition

bone material of inland residents C₃ consumer

land fauna animal meat birds, fresh water fish

100% from sea

50%

50%

100% from land (C₃)

δ¹³C (PDB) in %

-30

-25.7

-20

-19.6

-17.8

C₃ (-18.7)

-13.8

-7

-10

-0
Observations

Analysis of skeletons of early population of coastal British Columbia:
\[ \delta^{13}C = -13.4 \pm 0.9 \% \Rightarrow \approx 100\% \text{ seafood based nutrition} \]

Analysis of skeletons of early population of Ottawa region:
\[ \delta^{13}C = -19.6 \pm 0.9 \% \Rightarrow \approx 100\% \text{ } C_3 \text{ originated nutrition.} \]

Analysis of skeletons of early population of central British Columbia:
\[ \delta^{13}C = -15.4 \pm 0.3 \% \Rightarrow \approx 65\% \text{ seafood (salmon)} \& \approx 35\% \text{ } C_3 \text{ originated nutrition.} \]
Development of Mayan diet

From fish and vegetable towards maize dominated food

Demonstrated on a nitrogen/ carbon isotope ratio study

Belize: Stable Isotope Ratios in Human Bone Collagen
Meso-American food characteristics during the classical period

Local differences can be detected for isotope ratios in human bone collages.

Drastic differences due to corn of fish diet!
Checking on Yax K’uk Mo

5th century AD the City of Copan in southern Yucatan converted from a small village to a center of Mayan culture within only decades through installation of Yax K’uk Mo as local Rule (coronation 9. 5. 426 AD)

Origin of Yax K’uk Mo is unknown. Speculation that he was installed by Teotihuacán (Central Mexico) to extend political influence southwards.

Main indicator “Goggles”
Strontium Sr isotope ratio in upper incisor

Ratio $^{87}\text{Sr}/^{86}\text{Sr}$ is an important indicator for tooth analysis.

Strontium Sr behaves chemically similar to Calcium Ca in tooth enamel (formed during the early childhood). Sr can replace Ca by food intake. Isotopic ratio reflects origin.

$^{87}\text{Sr}/^{86}\text{Sr} = 0.7084$
Origin of $^{87}\text{Sr}/^{86}\text{Sr}$

Stable Strontium Sr isotopes:

- $^{84}\text{Sr}$ (0.56%)
- $^{86}\text{Sr}$ (9.86%)
- $^{87}\text{Sr}$ (6.94%)
- $^{88}\text{Sr}$ (82.58%)

$^{87}\text{Ru}$

$\beta$-decay

$T_{1/2} = 4.7 \cdot 10^{10}$ y

$^{87}\text{Sr}$

$^{86,87}\text{Sr}$ are stable isotopes, $^{87}\text{Sr}/^{86}\text{Sr} = 0.704$

Stable $^{87}\text{Sr}$ is enriched by decay of $^{87}\text{Rb}$.

An environment with high Rb content therefore causes high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio!
Yucatan peninsula formed by Ca/Rb containing Marine sediments $\Rightarrow$ $^{87}$Sr enrichment declining south.

Central Mexico is volcanic origin low Ca/Rb content
Recent Discoveries, the Iceman Oetzi

Isotope analysis of $^{18}O/^{16}O$ ratio in teeth shows much higher ratio than expected for high altitude origin. This indicates that Oetzi originates from low altitude country.

Comparison with characteristic isotope distribution in northern and southern alpine valleys clearly indicates that he originated from the southern valleys, now South-Tyrol in Italy. Ratios in bones indicate at least 20 years of high altitude habitat.
The Stonehenge Archer

Recent (2002) discovery of human remains (2300 BC) near Stonehenge
$^{18}$O/$^{16}$O distribution on the British Isles

Rain in coastal regions contains higher $^{18}$O abundance than rain. In continental regions ($^{18}$O weight)

$^{18}$O enriched at the rainy west coast!

\[
\delta^{18}O = \left( \frac{O^{18}}{O^{16}} \right)_{sample} \cdot 1000 \%
\]

\[
\left( \frac{O^{18}}{O^{16}} \right)_{SMOW}
\]
Tooth Analysis

Bronze tool expert, Import of know-how and knowledge???

Analysis indicates low $^{18}\text{O}/^{16}\text{O}$ ratio Much lower than typical for British Isles!

Ratio decreases with altitude and with distance from coastal area. The teeth show low ratio indicating high altitude, continental origin. Further comparison with other characteristic isotopes points towards alpine origin - northern Alp range.
Summary Isotope Analysis

The analysis of isotopic ratios is a rapidly emerging tool for provenance studies. It has a broad range of applications in history, archaeology, and anthropology. Isotope analysis studies can be performed with neutron activation techniques if the neutron capture products are radioactive and will emit a characteristic decay signal which can be easily identified and detected. In most cases, application of neutron activation techniques is insufficient for a thorough determination of all isotopic abundance ratios for an element. In these cases, isotope separators with high mass resolution and low sample mass requirements are the main tool for isotope analysis today.